(19) World Intellectual Property Organization International Bureau



(43) International Publication Date 11 July 2002 (11.07.2002)

PCT

(10) International Publication Number WO 02/053838 A1

- (51) International Patent Classification⁷: D21H 27/10, 19/82, 23/70, B65D 65/42, B32B 29/00, 31/30
- (21) International Application Number: PCT/US01/50809
- (22) International Filing Date:
 21 December 2001 (21.12.2001)
- (25) Filing Language:

English

(26) Publication Language:

English

US

US

US

(30) Priority Data:

60/258,686 28 December 2000 (28.12.2000) 60/298,868 15 June 2001 (15.06.2001) 09/896,552 29 June 2001 (29.06.2001)

- (71) Applicant: ROCK-TENN COMPANY [US/US]; P.O. Box 4098, Norcross, GA 30091 (US).
- (72) Inventor: GOULD, Richard, J.; 1859 Highland Parkway, St. Paul, MN 55116 (US).
- (74) Agents: KATZ, Mitchell, A. et al., Needle & Rosenberg, P.C., Suite 1200, The Candler Building, 127 Peachtree, N.E., Atlanta, GA 30303-1811 (US).

- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— ^ with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

12/053838 A1

(54) Title: GREASE MASKING PACKAGING MATERIALS AND METHODS THEREOF

(57) Abstract: The present invention relates generally to the packaging materials. More specifically, the invention relates to materials and methods suitable for use a s packaging materials whereby the appearance of grease, fat or oil staining on the packaging material is reduce or eliminated.

5

15

20

25

30

GREASE MASKING PACKAGING MATERIALS AND METHODS THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application No. 60/298,868, filed June 15, 2001. This application also claims priority to U.S. Provisional Application No. 60/258,686, filed December 28, 2000. The disclosures of each of these applications are incorporated herein by reference in their entireties.

10 FIELD OF THE INVENTION

The present invention relates generally to packaging materials. More specifically, the invention relates to materials suitable for use as packaging materials, whereby the appearance of grease, fast or oil staining on the packaging material is reduced or eliminated.

BACKGROUND OF THE INVENTION

Packaging materials, such as paperboard, paper or fabric are frequently utilized to package grease, fat or oil-containing materials. For example, human and animal foodstuffs commonly include a significant amount of grease, fat or oil. During filling, transport or storage, the grease, fat or oil from the foodstuff can migrate from the food product to the packaging material, thereby resulting in unsightly stains on the outer surface of the packaging material. Also, grease, fat or oil-containing materials may come into contact with the outer surface of the packaging material to cause staining. While this migration of grease, fat or oil does not normally effect the structural integrity of the packaging material, the consumer generally dislikes the stained container and may be less likely to purchase a product because of such staining.

One solution to the problem of grease, fat or oil staining on a packaging material is to place the material to be packaged within an separate impermeable container within the packaging material itself such as, for example, a plastic bag. While such a method normally prevents grease, fat or oil staining in the packaging material prior to use by the consumer of the packaged material, this method has less

effectiveness when the package has been opened and returned to the consumer's shelf for storage. For example, grease, fat or oil-containing crackers may be placed in a plastic bag within a packaging material. Grease, fat or oil will be contained within the bag as long as the bag remains closed. However, once opened, it is quite common for a consumer to drop one or more crackers between the bag and the inner surface of the packaging material when removing the crackers for use. If there is no barrier material between the outer surface of the plastic bag, it is likely that grease, fat or oil will migrate from the cracker into and through the packaging material, thereby resulting in an unsightly stain on the outer surface of the packaging material. Stains on packaging material may also be caused by filling line debris or puncturing of the plastic bag.

Stains on the packaging material may also be caused by contact by a grease, fat or oil-containing material with the outer surface of the packaging material. Such stains may be from contact of the package with a grease, fat or oil stain on another package or by contact with grease, fat or oil-containing substances that may occur during filling, transport or storage.

Furthermore, it will be understood that, irrespective of the origin of a grease, fat or oil stain, extended times and elevated temperatures will normally exacerbate the appearance of such stains.

Whether or not a plastic bag is placed within the packaging material, in the past, it has been common to treat the packaging material with a barrier material effective to reduce the possibility that grease, fat or oil will migrate into and through the packaging material to cause a visible stain on the outer surface of the packaging material. The most common barrier materials from the standpoint of cost and effectiveness have been those of the fluorochemical variety i.e., Scotchguard® products, made by the 3M Company of Minneapolis, MN. These materials have generally been applied to the packaging material prior to formation into, for example, a box. However, due to environmental and health concerns, 3M's fluorochemical barrier products have recently been removed entirely from the market. While other barrier materials exist, many otherwise effective methods are either not acceptable as the sole method of protection for use in certain applications or are applied from solvent-based systems. Moreover, for some of the more useful methods, the methods may be prohibitively expensive

5

10

15

20

25

and/or not effective enough for many applications. Thus, the removal of 3M's fluorochemical barrier products from use has left a major void in the packaging materials market.

U.S. Patent No. 4,521,492 discloses a method of masking the appearance of grease, fat or oil staining on a paperboard packaging substrate by first applying a nonleafing metallic ink over the substrate, followed by the application of a highly pigmented white outer layer. It is stated that the presence of the metallic ink alters the refractive index of the grease, fat or oil stained substrate and the over-coating with the highly pigmented white outer layer reduces or eliminates the metallic appearance of the lower ink layer. While effective for the masking of grease, fat or oil permeation, this method has at least two significant disadvantages. First, this material requires application of at least the non-leafing metallic ink layer using explosion-proof equipment because the non-leafing metallic ink is delivered from a solvent-based system. Second, the method requires the use of solvent recovery systems. These greatly increase the cost of utilizing this prior art grease masking system because the method cannot be used with existing mill equipment without resulting in difficulties. Further, the method of U.S. Patent No. 4,521,492 has limited applications to printing press methods which reduces the usefulness of the process in printing processes requiring a multiple of print stations.

Against the above, it would be highly desirable to develop a method whereby the appearance of grease, fat or oil staining on a packaging material could be masked so that even if grease, fat or oil staining does occur, such stains will be less noticeable. Specifically, it would be desirable to be able to mask the appearance of grease, fat or oil staining on a packaging material whereby the materials utilized do not comprise non-leafing metallic inks. Further, it would be desirable to apply such masking methods by way of aqueous systems, thereby allowing the use of standard mill equipment.

SUMMARY OF THE INVENTION

In accordance with the purpose(s) of this invention, as embodied and broadly described herein, this invention, in one aspect, relates to a packaging material comprising a substrate suitable for use as a packaging material wherein the appearance

5

. 10

15

20

25

of grease, fat or oil on the substrate is masked by the selection of the color and, optionally, composition of one or more colored layers proximally disposed on an outer surface of the substrate, wherein the substrate may itself be colored. In a further aspect, methods of making and using the previously described packaging materials are provided.

Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an illustration of a coated substrate with a dark colored layer and light colored layer disposed proximally thereto.

Fig. 2 is an illustration of a substrate in which the outer surface is dark colored and the substrate has a light colored layer disposed proximally thereto.

Fig. 3 is an illustration of a substrate with a precoat layer adjacent thereto and with a dark colored and light colored layer disposed proximally to the precoat treated substrate.

DETAILED DESCRIPTION OF THE INVENTION

Before the present compounds, compositions, articles, devices, and/or methods are disclosed and described, it is to be understood that this invention is not limited to specific methods of making or applying the masking compositions herein, or specific compositions thereof, and, as such, may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

20

25

It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the countext clearly dictates otherwise. Thus, for example, reference to "a colorant" includes mixtures of colorants.

Ranges may be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another embodiment. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

In this specification and in the claims that follow, reference will be made to a number of terms which shall be defined to have the following meanings:

"Colorant" means any substance that imparts color to another substance or mixture. As meant herein, white and black are colors. This definition of colorant also includes, but is not limited to pigments, dyes, whiting, barytes, clays and talc.

"Substrate color" means the color of the substrate e.g., paperboard, paper or fabric or other material without any added colorant and prior to the addition of the dark colored layer or the light colored layer. When a colorant is directly added to one or more plys of the substrate as described hereinbelow, the substrate color will be different from uncolored paperboard. For example, when recycled paperboard is the substrate, the substrate color will generally be light brown prior to the addition, if any, of colorant to one or more plys of the paperboard.

"Light colored" as utilized to describe either a layer or a colorant means having a value of from about 50 to about 95 on the Cielab scale. In further separate aspects, the light colored layer may be from about 55 to about 95 or from about 60 to about 95, or from about 65 to about 95, or from about 75 to about 95, or from about 80 to about 95, all such values being measured on the Cielab scale.

5

10

15

20

"Dark colored" as utilized to describe either a layer or a colorant means having a value of from about 0 to about 75 on the Cielab scale. In further separate aspects, the dark colored layer may be from about 0 to about 65, or from about 0 to about 55, or from about 0 to about 45, or from about 0 to about 30, or from about 0 to about 25, or from about 0 to about 20, or from about 0 to about 15, such values being measured on the Cielab scale.

As utilized herein, "dark colored" is defined in reference to a corresponding "light colored layer" and vice versa. That is, a dark colored layer (or substrate) is always darker in color that the light colored layer that will be applied over the dark colored layer (or substrate) when these two colored aspects combine to form the masking aspect of the present invention. In one or more aspects, it is possible that a dark colored layer (or substrate) utilized with one substrate may be lighter in color than the light colored layer utilized on a different substrate.

"Aqueous" means that the system comprises about 92% by weight or above of water. Such systems are considered to be essentially solvent free.

"Proximal" means that the referenced aspect or object is near to but not necessarily touching the aspect or object to which the word "proximal" refers. "Adjacent to" means the aspect or object is touching the aspect or object to which the phrase "adjacent to" refers.

References in the specification and concluding claims to parts by weight of a particular element or component in a composition or article, denotes the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a compound containing 2 parts by weight of component X and 5 parts by weight component Y, X and Y are present at a weight ratio of 2:5, and are present in such ratio regardless of whether additional components are contained in the compound. However, compositions such as those disclosed and claimed herein may also be described by one of ordinary skill in the art as containing "parts" of a component. For example, a composition containing 100 parts pigment and 22 parts binder would comprise 82%

5

10

15

20

25

1.7

. 17

.74

بالب

ίť-

٠,,٠

. . <u>. . .</u> . .

•>

40.

30

pigment (100/100+22) and 18% binder (22/22+100). Such nomenclature is not used to describe and claim the invention herein.

A weight percent of a component, unless specifically stated to the contrary, is based on the total dry weight percent of the formulation or composition in which the component is included.

As utilized herein, "packaging material" means a material that may be used to make an article suitable for performing one or more of the following functions: a) containment for handling, transportation and use; b) preservation and protection of the contents for required shelf and use life and sometimes protection of the external environment from any hazards of contact with the contents; c) identification of contents, quantity, quality and manufacturer; and d) facilitation of dispensing and use. Non-limiting examples of the packaging material article include a wrap, pouch, bag, box, cup, tray, plate, can, tube, bottle or other container form.

By the term "effective amount" of a compound or property as provided herein it is meant such amount as is capable of performing the function of the compound or property for which an effective amount is expressed. As will be pointed out below, the exact amount required will vary from process to process, depending on recognized variables such as the compounds employed and the processing conditions observed. Thus, it is not possible to specify an exact "effective amount." However, an appropriate effective amount may be determined by one of ordinary skill in the art using only routine experimentation.

Referring first to the drawings, Fig. 1 is an illustration of one aspect of the present invention. A substrate 12 having an inner substrate surface 14 and an outer substrate surface 16 is coated with a dark colored layer 18 having an inner dark colored surface 20 and an outer dark colored surface 22 such that the dark colored layer is disposed proximal to outer substrate surface 16. A light colored layer 24 having an inner light colored surface 26 and an outer light colored surface 28 is disposed proximally to outer dark colored surface 22. A packaged good 30 may be present and may or may not be in contact with the inner substrate surface 14.

5

10

15

20

Fig. 2 illustrates a further aspect of the present invention wherein the substrate 32 has an integrated dark colored portion 34 having an inner dark colored surface 36 and an outer dark colored surface 38. The light colored layer 24 may then be disposed proximally to the outer dark colored surface 38.

Fig. 3 illustrates a further aspect of the present invention wherein the substrate 12 has a precoat layer 40 having an inner precoat surface 42 and an outer precoat surface 44 disposed proximally to outer substrate surface 16 and inner dark colored surface 20.

Now referring to a first major aspect of the present invention, the invention provides a material for packaging grease, fat or oil-containing substances, wherein the packaging material comprises: a grease, fat or oil permeable substrate suitable for use as a packaging material, wherein the substrate has an inner and an outer surface; a dark colored layer having an inner and outer surface disposed proximal to the outer surface of the substrate, wherein the dark colored layer comprises a dark colorant; and a light colored layer having an inner and an outer surface disposed proximal to an outer surface of the dark colored layer, wherein the light colored layer comprises a light colorant; wherein the dark and light colored layers are selected to mask the appearance of grease, fat or oil staining on the packaging material, and wherein neither the dark colored layer nor the light colored layer comprises a non-leafing metallic ink. By "nonleafing metallic ink," it is meant the inks disclosed in U.S. Patent No. 4,521,492, the disclosure of which is incorporated herein in its entirety by this reference. In a still further aspect, the colorants of the invention herein do not comprise a metallic material. For example, the colorants of the invention herein do not comprise an aluminumcontaining colorant. Yet still further, the colorants of the present invention consist essentially of a non-leafing metallic ink.

A grease, fat or oil-containing material can be packaged in the packaging material. Upon storage, grease, fat or oil from the packaged material may come in contact with the inner surface of the substrate such that grease, fat or oil may migrate through the substrate to be visible on an untreated outer surface of the substrate. Also, grease, fat or oil may come into contact with the outer surface of a packaging material during filling or storage of the packaging material. It has been discovered that with the

5

10

15

20

25

present invention, the appearance of such grease stains may be reduced or eliminated. As meant herein, "reduced" or "eliminated" are terms that will be relative to the specific application. For example, in a particular aspect, grease, fat or oil staining may be totally "eliminated" when the package has a useful life of only several weeks, whereas, grease, fat or oil staining may be "reduced" in the same treated substrate if the useful life of the package is several months. This is due to the fact that the present invention generally does not result in the formation of an impermeable barrier on a packaging material. Rather, it is believed that through a combination of optical phenomena and formulation selection, the surprising and unexpected masking properties of the present invention are obtained.

In a further aspect, the dark colorant may comprise one or more of: carbon black, raw sienna, burnt sienna, burnt umber, chrome black, high purity furnace black, black azo dyes or brown azo dyes. In a still further aspect, the dark colorant comprises carbon black. While such masking many not be permanent in most circumstances, the duration and extent of masking is sufficient for pacinaging materials uses.

In a further aspect, the light colorant comprises one or more of: titanium dioxide, calcium carbonate, calcium silicate, calcium sulfate, barium sulfate, natural clay, a synthetic clay, magnesium oxide, magnesium silicate, zinc carbonate, zinc oxide and plastic pigment. A titanium dioxide product particularly suitable for use in the invention herein is Huntsman R-BC Slurry, a product of Huntsman Trioxide, Salt Lake City, UT. Clays suitable for use in the invention herein include, but are not limited to, kaolin (grades 1, 2 etc.), dellaminated clay and structured clay. Kaolin clays particularly suited for the invention herein include Kaoprint and Kaobrite, products of Thiele, Sandersville, GA. In a further aspect, the colorant does not comprise calcium carbonate.

In a further aspect, the dark colorant may be optionally applied from a dark colorant-containing solution. It should be noted that the dark colorant-containing solution may normally contain additional materials, including other colorants. These additional materials may comprise materials such as titanium dioxide, which, in addition to being a white colorant, may also act as an opacifier. Thus, when opacity is desirable in the dark colored layer, titanium dioxide can be included along with the dark

10

15

20

25

colorant. A further additional material in the dark colored layer, as well as in the light colored layer, may comprise clay or calcium carbonate, which, in addition to being white colorants, may also act as extenders or opacifiers, whereby the amount of colorant to be utilized in the solution may be reduced or eliminated. Thus, it is contemplated according to the invention herein, that the dark colorant-containing solution may also contain materials that are referred to elsewhere herein or otherwise known as "light colorants" or that are otherwise generally known to one of ordinary skill in the art as "colorants." Thus, when utilized in conjunction with the dark colorant herein, the purpose of these materials is for a reason other than for conferring color, however, some color may nonetheless be conferred by use of such materials.

In a significant aspect, the materials utilized in one or more of the dark or light colored layers or to color one or more plys of the substrate itself may be suitable for use in food, drug or cosmetic applications. Such materials are specifically described in Title 21 of the United States Code. More particularly, the colorants that may be suitable for use in the invention herein are described in Title 21, Section 178.3297 of the United States Code. The disclosures of all referenced United States Code sections are herein incorporated in their entireties by this reference. Other materials, whether colorants or otherwise, may be suitable for use in food, drug and cosmetic applications that are not specifically delineated in the United States Code, particularly materials that may be available outside of the U.S. and are suitable for use therein. As such, it is contemplated herein that materials not specifically set forth in the United States Code may be utilized in the present invention.

One of ordinary skill in the art may further understand that other non-food, drug or cosmetic approved colorants or other ingredients may be utilized in accordance with the invention herein according to the intended end-use for the packaging material, as long as such colorants are not those utilized in non-leafing metallic inks. For example, if the material to be packaged is a grease, fat or oil-containing pesticide, it will not be necessary for the materials utilized on the surface of the packaging substrate to be acceptable for food, drug or cosmetic applications. Further, even where the material to be packaged is food, drug or cosmetic material, a wide range of additional colorants may be utilized where such materials are acceptable for such applications.

10

15

20

25

In one aspect, the dark colored layer may be applied from a dark colorant-containing solution, wherein the dark colorant-containing solution comprises from about 0.01 to about 20.0 % by weight of the dark colorant as measured by total weight of the solution. Still further, the dark colorant-containing solution comprises from about 0.25 to about 4.0 % by weight of the dark colorant as measured by total weight of the solution. Yet still further, the dark colorant may be present in the dark colorant-containing solution at from about 0.01, 0.1, 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 10.0, 12.0, 14.0, 16.0, 18.0 and 20.0% by weight of the dark-colorant-containing solution, where any of these stated amounts may comprise either the upper or lower endpoint of the range of dark colorant therein and any lower endpoint can be used with any upper endpoint.

In a further aspect, the light colored layer may be applied from a light colorant-containing solution, wherein the light colorant-containing solution comprises from about 30 to about 90 % by weight of the light colorant as measured by total weight of the solution. Still further, the light colored layer may be applied from a light colorant-containing solution, wherein the light colorant-containing solution comprises from about 40 to about 80 % by weight of the light colorant as measured by total weight of the solution. Yet still further, the light colorant may be present in the light colorant-containing solution at from about 1, 5, 10, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 99 % by weight of the light colorant-containing solution, where any of these stated amounts may comprise either the upper or lower endpoint of the range of light colorant therein and any lower value can be used with any upper value.

In a significant further aspect, either or both of the colored layers may be applied from respective light or dark colorant-containing solutions, wherein either or both solutions may be aqueous. By having aqueous systems as defined previously, standard paper mill equipment may be readily utilized to prepare packaging materials according to the invention herein. This provides significant advantages in the present invention over the methods disclosed in U.S. Patent No. 4,521,492.

In one or more aspects of the present invention, the dark colored layer may not be separately applied to the substrate. If no dark colored layer is separately applied, the substrate itself may have a substrate color that is darker than the light colored layer. In

5

10

15

20

25

such an aspect, the substrate color is modified to be darker than the uncolored (natural) substrate. For example, a dark color can be added to one or more layers (or plys) in a single or multi-ply paperboard by means of a colorant addition step during the paper manufacturing process so that the entire substrate (in a single ply product) or the outer surface of the paperboard (in a multi-ply product) is darker than that of uncolored substrate. In one aspect, a multi-ply paperboard article may be manufactured whereby the pulp comprising one or more outer plys, for example, the top liner, is treated with a dark colorant to result in a dark colored outer surface for the substrate. In separate aspects, the number of plys in the paperboard (whether colored or uncolored) is two, three, four, five, six, seven, eight, nine or ten, in which one or more outer plys may be colored with a dark colorant according to the present invention. Such dyes or colorants may be present in a pulp slurry in a range of from about 0.1 to about 3.0 % by weight. Such colorants may in the form of azo dyes wherein the individual colors may be used alone or mixed with other azo dyes to form a dark color in one or more plys of the paperboard. In a further aspect, the entire paperboard product may be dark colored by the addition of azo dyes to a pulp slurry in the amounts of from about 0.1 to about 3.0% by weight.

Methods of making paperboard products are not crucial to the invention herein and are well known generally to one of ordinary skill in the art. Specific examples of methods that may be utilized herein are described generally in U.S. Patent Nos. 4,753,710, 4,913,773 and 5,169,496, the disclosures of which are each incorporated herein in their entireties by this reference.

3

.....

. 1

As contemplated herein, the specific shade of dark colorant or light colorant is not crucial to the invention. However, as noted, the "dark" colorant should provide a color to the substrate that is darker than that provided by the "light" colorant to the light colored layer and vice versa.

In one aspect, the light colored layer may be white and the dark colored layer may be black or gray. In further aspects, the light colored layer may be yellow, pink, pale green, pale blue, etc.; that is, the light colored layer may be any color that exhibits a significant reflectance of light. The dark colored layer may be blue, purple, brown, etc.; that is, the dark colored layer may be any color that exhibits a significant

5

10

15

ä.

` 20

25

absorbance of light. Definitions of "light colored" and "dark colored" are as previously set forth herein.

While not wishing to be bound by theory, it is believed that by selecting an outer substrate color that is closer in color to that of a grease, fat or oil stain, the appearance of a grease, fat or oil stain on the outer surface of the packaging material will be lessened, reduced or eliminated. That is, it is hypothesized by normalizing the background color of the packaging material to a shade similar to the grease, fat or oil, the refractive index of the packaging substrate may be altered so that a grease, fat or oil stain may be less visible in the finished packaging material. Further, selection of the light colored layer will be dependent on a number of factors including the degree of darkness of the dark colored layer and the desired whiteness/brightness of the outer layer.

It should be noted that a very dark colored layer itself will likely be effective to mask a wide variety of grease, fat or oil stains or a substrate. However, one of ordinary skill in the art will recognize that such a dark layer will be difficult to cover with a light-colored over layer without having a very thick layer and/or having a large amount of opacifying pigments, such as TiO₂. However, according to the method and compositions of the present invention, it is possible to mask grease, fat or oil staining by means of selection of the dark colored and light color layers to provide cost effective packaging materials.

Accordingly, when a light colored layer is selected and applied over the dark colored substrate or the dark colored layer, the masking may be effectuated by the application of the light colored outer layer. In accordance with the present invention, and in some aspects in conjunction with binder materials (as discussed in more detail below), it is believed that this optical phenomenon is augmented and enhanced in a surprising and unexpected manner.

In the selection of the colors so as to mask the appearance of grease, fat or oil permeation (e.g. staining) in a packaging material, the relative thickness of the colored layers, the concentration of colorants in the coatings, the type off grease, fat or oil-containing material being packaged and the time and the temperature to which the

ः ३

. .

15

20

25

package is subjected will each be relevant. For example, when the grease masking capability of a packaging material need only be apparent for a short time, such as with a fast food container in which the packaged material may be consumed shortly after purchase, a dark color may not need to be as dark and a light color may not need to be as light relative to each other because the grease masking necessity for the package is relatively short-lived. In contrast, when packaging a food product where the storage capability needs to be longer, the dark color and/or the light color may need to have a greater masking ability. Moreover, the degree of a grease, fat or oil stain will also be related to the type of material being stored in the packaging material. However, in accordance with the disclosure herein and the general knowledge in the art, one of ordinary skill in the art will be able to determine the relative amounts of ingredients, thickness of coatings, etc. useful for particular applications without undue experimentation.

In a still further aspect, the packaging material may have a TAPPI brightness number of from about 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99 or 100, where any of these referenced measurements may comprise either the upper or lower endpoint and any of these lower endpoints may be used with any of these higher endpoints. In a further aspect, the packaging material may have a TAPPI brightness number of from about 60 to about 90. Still further, in another aspect, the packaging material has a TAPPI brightness number of greater than 75. The brightness of the packaging materials are measured according to TAPPI method T452 om-83. This TAPPI method is incorporated herein in its entirety by this reference.

In a further major aspect, the grease, fat or oil permeable substrate utilized according to the compositions and methods herein comprises paperboard, paper or fabric. However, one of ordinary skill in the art will recognize that the substrates in which this invention may be utilized are not limited to these specifically enumerated substrates. Rather, it is contemplated according to the invention herein "substrate" includes any article that customarily or feasibly could be coated with a coating formulation or that may itself be dark colored and may be coated with the light colored layers described herein. In separate aspects, the substrate must be suitable for use as a packaging material as the term is defined elsewhere hereim.

5

10

15

20

25

30

5

10

15

20

25

30

Still further, in another aspect, the grease, fat or oil permeable substrate may comprise paperboard. The paperboard so utilized can specifically comprise one or more of: SBS ("solid bleached sulfate"), SUS ("solid unbleached sulfate") or recycled paperboard.

SUS (for example, Omnicoat® or Pearlcoat®, Riverwood, Marietta, GA) utilized according to the methods herein may be comprised of primarily southern pine species such as the Loblolly as a fiber source, although some hardwood fiber may be used, particularly in one or more outer plys. Some recovered paper may also be added as a fiber source, which may account for about 20% of the fiber (although this amount will vary based on market conditions and other factors). SUS is generally a brown-colored paperboard which can then be coated according to the methods herein with application of a dark colored layer proximal to the SUS and a light colored proximal to the dark colored layer. Additionally, one or more outer plys of the SUS may be colored to result in a one or more dark colored outer plys on the paperboard.

When recycled paperboard (for example ClassicNews®, Rock-Tenn Company, Norcross, GA) is utilized in the compositions and methods herein, a variety of types of recovered paper and paperboard may be utilized. Each source may have an impact on the final substrate and, accordingly, the packaging applications to which the packaging material is suited. Two of the predominant fibers utilized in recycled paperboard sources may be old newspapers (ONP) and old corrugated containers (OCC). ONP normally add bulk and can improve formation but may not convey as much strength as OCC. Another common fiber source may be office waste paper (OWP) which has high value when utilized as an outer (top) ply to provide a clean, smooth printing surface for the coated recycled paperboard. This outer ply may be made dark colored according to the methods of the invention herein. Recycled clippings from printing and converting plants also can provide a large fiber source for the recycled coated paperboard industry.

SBS (for example, from Westvaco, Covington, VA) that may be utilized according to the methods and compositions herein generally comprises bleached fiber from both softwood and hardwood trees, although there normally is a higher percentage of hardwood fiber therein. The percentage of hardwood fiber can vary significantly without affecting its use in the invention herein, but, typically, the hardwood content

may be greater than about 80%. SBS utilized according to the methods herein may also contain some recycled fibers. When matted into paperboard according to known papermaking procedures, hardwood fibers generally form a smooth white sheet. As such, without treatment with the grease masking method herein, the appearance of grease, fat or oil staining on this SBS substrate will be marked.

In a significant aspect, the packaging material prepared according to the invention herein may be suitable for use in packaging food, drugs or cosmetics. More particularly, the packaging material may be suitable for use in packaging human food or animal food.

In addition to paperboard as described above, the substrate may be paper or fabric. If the substrate is paper or fabric or some other suitable substrate, it will be understood that the substrate itself may be dark colored or a separate dark colored outer layer may be applied to accomplish the objectives of the present invention. When paper, the packaging material may be in the form of a single layer or in a multi-ply bag. Application of the dark and hight cohored layers to both paper and fabric materials is in accordance to the methods disclosed herein with respect to paperboard. To the extent that the application methods may differ, such differences will be minimal and one of ordinary skill in the art will recognize the same.

In a further aspect, the colorant-containing solutions from which one or more of the dark colored layers and the light colored layers are applied each, independently, comprise one or more of: water, dispersant, resin, surfactant, wetting agent, defoamer, thickener, starch, preservative, or amtioxidant. Such additional materials may be included in the colorant-containing solutions according to methods known generally to one of ordinary skill in the art. Non-exclusive examples of coating formulations that may be utilized in accordance with the invention herein are disclosed generally in U.S. Patent No. 5,837,383, the disclosure of which is incorporated herein in its entirety by this reference.

Furthermore, there may be a layer on the outer surface of the grease, fat or oilpermeable substrate, wherein the layer comprises one or more of: starch, polyvinyl alcohol, or one or more sizing agents that would be recognizable by one of ordinary

5

10

15

20

25

5

10

15

20

25

30

skill in the art. When starch is utilized in the present invention, the starch may be catatonically modified to augment the affinity of the precoat to the substrate that, if comprised of paper or paperboard, may carry a net anionic charge. Still further, in another aspect, the layer may comprise a dye, pigment or other type of colorant, and, as such, this layer may operate as the dark colored layer. This layer, whether colored or not, may or may not comprise binder.

Still further, in another aspect, a printed layer may be present adjacent to an outer surface of the light colored layer. Such methods of printing are well known to one of ordinary skill in the art and, as such, are not described herein in detail.

With respect to the dark colored layer aspect of the invention, the following method may be utilized. After preparation and drying of the packaging substrate, a dark colorant containing solution, for example, comprising starch, dark colored pigment and water can be applied on a wet stack calendar (in addition to or instead of applications on a size press for Fourdrinier machines). The wet stack may consist of a stack of rollers, which may be from five or seven rollers high. The web may then be threaded through this stack. Water boxes containing the percent solution may be placed adjacent to one roller for the topside of the web and another roller for the bottom side of the web. The dark colored layer can be applied to the web as the web passes the water boxes.

In separate aspects, the dark colored layer may be adjacent to the substrate and the light colored layer may be adjacent to the dark colored. Still further, the dark colored layer may be proximal to the substrate and adjacent to the light colored layer. Still further, the dark colored layer may be proximal to the substrate and the light colored layer may be proximal to the dark colored layer.

In addition to the previously described layers, a barrier or fixing layer separate from the light and or dark colored layer may be added at any location on the packaging material without detracting from the purposes of the present invention. For example, a clear barrier or fixing coat may be disposed between the outer surface of the substrate and the dark colored layer, between the dark colored layer and the light colored layer or may be disposed on the surface of the light colored layer before or after the application

of a printed layer, if any.

5

10

15

20

25

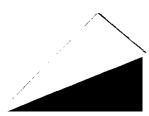
30

BNSDOCID: <WO 02053838A1 1 3

As noted, binders may be useful in the light and/or dark colorant-containing solutions herein and will be present in binder solutions as binder solids as discussed below. Binders suitable for use in the first or light colored solutions herein may comprise naturally- or synthetically-derived materials.

In particular aspects, suitable synthetic binders may comprise latex polymers. wherein such latex polymers are derived from monomers comprising one or more of: acetoacetoxy ethyl methacrylate, acetoacetoxy ethyl acrylate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, ethylhexyl acrylate, 2-ethylhexyl methacrylate, 2-ethyl hexyl acrylate, isoprene, octyl acrylate, octyl methacrylate, iso-octyl acrylate, iso-octyl methacrylate, trimethyolpropyl triacrylate, styrene, α-methyl, glycidyl methacrylate, carbodiimide methacrylate, C₁-C₁₈ alkyl crotonates, di-n-butyl maleate, αor-β-vinyl naphthalene, di-octylmaleate, allyl methacrylate, di-allyl maleate, diallylmalonate, methyoxybutenyl methacrylate, isobornyl methacrylate, hydroxybutenyl methacrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, vinyl acetate. vinyl ethylene carbonate, epoxy butene, 3,4-dihydroxybutene, hydroxyethyl(meth)acrylate, methacrylamide, acrylamide, butyl acrylamide, ethyl acrylamide, vinyl(meth)acrylates, or isopropenyl(meth)acrylate. In particular, suitable latexes may include one or more of: styrene butadiene (SBR), polyvinyl acetate, polyvinyl acetate-acrylate, ethylene vinyl acetate, styrene acrylates, polyacrylates and acrylic materials. Still further, naturally derived binders may be used in the present invention. Such binders may include, but are not limited to, soy or animal protein materials.

One of ordinary skill in the art will recognize that such binders may be useful in the methods of the present invention to assist in holding the colorant particles together and to the packaging substrate. The type of binder utilized in the methods of the present invention may vary depending on the particular colorant utilized, the packaging substrate and the intended end use for the packaging material. For example, SBR binders typically provide very good binding strength, gloss, ink holdout, and flexibility. PVAc binders can provide good gluing properties, brightness stability, ink receptivity,



5

10

15

20

25

30

and low odor. Protein binders may contribute to appearance, gloss, fountain solution acceptance, and glueability.

As for binder amounts to be included in the solutions, a binder may be present in the dark and/or light colorant-containing solutions in an amount of from about 17 to about 60 % by weight of each individual colorant-containing solution. Still further, the binder may be present in the dark and /or light colorant-containing solutions in am amount of from about 17 to about 37 % by weight of each individual colorantcontaining solution. Still further, the amount of binder may be from 23% to 40% by weight of each individual colorant-containing solution. The further aspect, the binders may be present at from about 25% to about 35% by weight of each incivious conformation containing solution. Still further, the binders may be present in the individual collorantcontaining solutions in the amount of from about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65 or 70 % by weight of each individual colorant-containing solution, where any of these values may form the lower endpoint and the upper endpoint and any lower value may be utilized with any upper value. In a further aspect, the amount of binder is greater than 17% by weight. One of ordinary skill in the art will recognize that such binder materials are often supplied as % solids in liquid. The values recited herein are measure as total dry weight under solids used in the coating compositions.

In further aspects, a mixture of synthetically and naturally derived binders may be utilized in the individual colorant containing solutions. In one non-limiting aspect of the invention, the individual colorant containing solutions may comprise a mixture of latex polymer binder and animal and/or vegetable protein, wherein the total amount of binder in the acting composition is measured by the sum of the weight percent of latex polymer solids and the soy protein solids. In a further aspect, the ratio of latex polymer to animal and/or vegetable protein is from about 2:1 to about 20:1, or from about 2:1 to about 10:1, where the total amount of binder in the individual colorant containing solutions is as stated previously. Still further, the ratio of latex polymer to animal and/or vegetable protein is from about 7:1 to about 12:1, where the total amount of binder in the individual colorant-containing solutions is stated previously. Yet still further, the ratio of latex polymer to animal and/or vegetable protein is from about 3:1, 5:1, 7:1, 9:1, 10:1, 11:1, 13:1, 15:1, 17:1, 19:1, where any lower value may be paired with any upper value and where the total amount of binder in the individual colorant-

containing solutions is as stated previously.

10

15

20

25

30

BNSDOCID: -WO 02052828A1 I -

In one aspect, the dark colored layer does not comprise binder and the light colored layer comprises binder. In a further aspect, the dark colored layer comprises binder and the light colored layer does not comprise binder. Still further, in another aspect, each of the colored layers comprise binder.

Although the amounts of components in the individual colorant solutions are recited above, it should be noted that the amount of pigment, binder and/or other ingredients, will be, in part, affected by factors such as the base color of the substrate and the amount and duration of the grease masking needed in a particular application. For example, where recycled paperboard or SUS board stock is utilized as a substrate, the base color of the substrate will be darker (or less white). Accordingly, the amount of pigment in the light colored layer(s) may need to be higher in order to satisfactorily hide the color of the substrate. In contrast, if SBS is utilized as the substrate, the amount of light colored pigment needed in the light colored layer(s) may be lower than that needed for a darker colored substrate because this substrate is less dark in color.

Moreover, while the specific type of binder(s) utilized in the present invention has not been found to be crucial to the present invention, one of ordinary skill in the art would recognize that the amount of pigment in the colorant containing solutions should directly affect the amount of binder to be included in the solutions. Thus, where a lower amount of light colored pigment is utilized (as discussed above), a proportionally lower amount of binder will be necessary. However, in accordance with the grease, fat or oil masking compositions and methods of the present invention, the amount of binder needed for a particular application has been found to be in excess of the amount of binder utilized for that same particular application where no grease, fat or oil masking properties are present.

The dark and light colored layers may be applied utilizing existing methods of applying coatings to packaging substrates. Such methods and compositions useful herein are known generally to one of ordinary skill in the art of packaging material manufacture and, as such, are not described in detail herein. Methods and compositions that may be utilized according to the invention herein are disclosed in U.S. Patent Nos.

3,196,038, 3,873,345, 4,265,969 and 4,301,210, the disclosures of which are each incorporated herein in their entireties by this reference.

Further specific examples of coating methods that may be utilized include the following.

- 5

. 10

15

20

25

In a major aspect, an in-line coating method maybe utilized to reduce the cost of the coating process, however, in another aspect an off-line process may be utilized. Coating processes that may be utilized include, but are not limited to: roll coating, rigid blade, straight blade or bent blade, air knife or a combination of coaters. Additionally, the compositions of the invention may be applied utilizing rotogravure and flexographic methods.

Roll coaters will generally not be utilized as a stand-alone coating method but may be used as the applicator roll in each of the coating processes discussed below. One of ordinary skill in the art will recognize that roll coaters operate similarly to a roller one uses to paint a wall at home. That is, in one aspect, the roll may rotate in a vat of coating and continues to rotate until it comes into contact with the paperboard and applies the wet coating thereto. The wet coating may then immediately be removed by either a blade, rod, or air knife.

A blade coater may be utilized to remove excess coating by use of a rigid (straight) or bent blade. In either aspect, the blade may actually contact the paperboard and scrape off the excess coating. Blade coaters will generally leave more coating in the low areas (valleys) and less coating on the high areas (hills) of the paperboard.

Blade coatings may be utilized to level off and seal the paperboard. Blade coatings generally augment paperboard smoothness and may be preferable for some end uses. A typical blade coater will generally apply from about 1 to 2 dry pounds of coating per 1000 square feet. Blade coaters are generally utilized to apply base coating (primers) as well as top coatings to seal the sheet. Blade coaters are particularly useful when the packaging substrate utilized herein is SBS.

A rod coater may be utilized according to the invention herein to remove excess coating with a smooth or wire wound rod. The rod may be placed in a holder and may

5

10

15

20

25

30

BNSDOCID: <WO 0205383841 L >

ء - پائ be slowly rotated as coating is wiped away. One of ordinary skill in the art will recognize that a rod coater operates similarly to a blade coater in that it generally levels and seals the sheet, but may also follow the natural contour of the paperboard surface. Rod coaters can be considered to allow a greater margin for error than a blade coater, in that small impurities that can cause scratches and streaks in the blade process are more likely to pass under the rod and not cause these defects. For this reason, rod coaters will be useful in the present invention when the packaging substrate comprises recycled paperboard and or SUS. Rod coaters will generally apply from about 1 to 3 dry pounds of coating per 1000 square feet.

In a further aspect, an air knife coater may be utilized to remove excess dark and/or light colored layer by the blowing of a thin jet of air on the wet coating. The air knife generally leaves a more uniform film thickness of coating across the entire web by following the contour of the sheet. Thus, if the surface of the packaging substrate is rough, it will remain rough. If it is smooth, it will generally remain smooth. Because of its excellent uniformity and its greater thickness, air knife coatings may be utilized when an opaque coating is desired. Air knife coatings are particularly useful for coating SBS and recycled paperboard. Typical air knife coaters will generally apply about 2 to about 6 dry pounds of coating per 1000 square feet.

In accordance with the methods herein, two, three or more coating units may be utilized to prepare the packaging material. In one aspect, the use of multiple coating methods may allow improved smoothness of the surface of the packaging material and may generally allow improved printability. One of ordinary skill in the art will recognize that various combinations may be utilized depending on the characteristics of the packaging substrate and the performance and cost attributes desired in the finished packaging material.

It will be recognized that when applied from a colorant-containing solution, the one or more colored layers are applied wet and should normally be dried. Drying of the packaging materials can be accomplished using either forced air or infrared dryers. In some cases both methods may be used.

In a further aspect, the coated packaging material may be dry calendered either

5

10

.15

20

25

30

before or after the application of a printed layer, if one is desired. One of ordinary skill in the art will recognize that dry calendering is a process of polishing the coated substrate and of controlling caliper and density of the finished surface. Calender finishing is generally performed to improve smoothness and increase gloss of the finished packaging material. In accordance with the present invention, a stack of calendar rolls may be utilized; this is generally referred to as "hard nip calendering." Alternatively, gloss calenders having a highly-polished, heated cylinder that is loaded against a resilient rubber backing roll may be utilized. As the packaging substrate outer surface comes into contact with the polished hot roll and enters the calender nip (between the two rolls), a slight change in speed may occur which results in a polishing of the coating. This process is referred to as "soft nip calendering." Methods of calendering are known generally to those of ordinary skill in the art. Non-exclusive examples of calendering are disclosed in U.S. Patent No. 5,029,521, the disclosure of which is incorporated herein in its entirety by this reference.

In a further major aspect of the invention herein, the dark colored layer and light colored layer each, independently, may comprise one or more of: polyethylene, polyester, polypropylene, polystyrene, or halogenated or non-halogenated vinyl polymers. Such materials may also be considered, in some aspects, to comprise binder materials. With respect to the polyethylene aspect, suitable polyethylenes include HDPE, MDPE, LLDPE, homogenously branched linear ethylene polymers and substantially linear ethylene polymers. Such materials may also be considered, in some aspects, to comprise binder materials. In this aspect, the dark colored layer and the light colored layer each, independently, may comprise from about 5 to about 40 %colorant as measured by total weight of each individual layer. Still further, the dark colored layer and the second layer each, independently, may from about 5, 10, 15, 20, 30, 40, 45, and 50 % colorant, where any of these numbers may comprise either endpoint for the amount of colorant and any lower endpoint may be utilized with any upper endpoint. While any of the above-described colorants may be utilized in this aspect of the invention, in one further particular aspect, the light colorant may comprise titanium dioxide and the dark collorant may comprise carbon black.

In this aspect of the invention, a grease, fat or oil permeable substrate having an outer surface is provided whereby a dark colored layer may be extruded onto the outer

surface of the substrate and a hight colored layer may be simultaneously or sequentially extruded onto an outer surface of the dark colored layer. Alternatively, a paperboard material may be utilized wherein one or more layers (plys) of the paperboard are colored with a dark colorant. In this latter aspect, a one or more colored layers may be extruded onto the outer surface of the colored paperboard with or without application of a precoat layer.

Methods of extrusion coating packaging materials are known generally to one of ordinary skill in the art, and, as such, need not be described in detail herein. Non-exclusive examples of extrusion coating methods that may be utilized according to the invention herein are described generally in U.S. Patent Nos. 4,343,858 and 4,455,184, the disclosures of which are each incorporated herein in their entireties by this reference.

In a further aspect, one or more of the colored layers may be extruded either simultaneously or sequentially to form a laminate material. This laminate material may be applied to the outer surface of the substrate of the invention herein to form either or both of the colored layers.

In still a further aspect, a dark colored layer may be applied to the substrate and a light color layer may be extruded to the dark colored surface. For example, a dark colored layer having an inner and an outer surface may be applied from a dark colorant-containing solution as set forth above. A light colored layer having an inner and an outer surface may then be extruded thereto. Alternatively, a dark colored paper or fabric may be applied to a paperboard, paper or fabric substrate and a light colored layer extruded thereto.

The substrates treated according to the present invention may be utilized in a number of different applications. In specific non-limiting examples, packaging materials in the form of a box, cup, tray, plate, can, tube, bottle or other container form may be prepared. Materials packaged therein may be consumer goods. In separate examples, the packaging materials may be used for both food and non-food packaging. As examples of food that may suitably be packaged in materials treated with the compositions and methods of the present invention, the following non-limiting

5

10

15

20

25

examples are presented: sweets, chocolate, confectionery, pastries, biscuits, dairy products (e.g., butter and cheese), powdery foodstuffs (e.g., coffee, tea, cocoa, flour, cereals), frozen food (e.g., ice cream, pastries, vegetables, seafood), fresh and semipreserved foods, pet food or carryout foods. Non-limiting examples of non-food packaging that may suitably be packaged in materials treated with the compositions and methods of the present invention include: cosmetics, toiletries, pharmaceuticals, cigarettes, detergents, textiles, toys, games, tools, household appliances, pesticides, fertilizers, hobby items, paper products, cassettes, record sleeves, and auto parts.

Converting methods known generally in the art may be utilized to form the packaging materials of the present invention. For example, the packaging material may be fabricated into a box configuration, a tube (shell) configuration, a tray configuration, or a bottle wrap configuration. These recited examples are meant to be illustrative only and one of ordinary skill in the art would recognize that the types of packaging materials that may be fabricated utilizing the grease, fat or oil masking compositions of the present invention may encompass a wide variety of configurations. Moreover, one of ordinary skill in the art would recognize conventional converting methods (i.e., cutting, creasing, and gluing) are suitable for use in conjunction with the present invention.

EXPERIMENTAL

10

15

20

25

30

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices, and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °F or is at ambient temperature, and pressure is at or near atmospheric.

Bending chip recycled paperboard ("uncoated box board") was utilized in the examples.

Suitable formulations for use in the present invention are set forth in Tables 1 and 2 below.

Various grease, fat or oil-containing packaged goods were tested in packaging materials treated with formulations of the present invention, such as those described below. Such tests were run for extended times and at elevated temperatures as described.

All tests utilized grease, fat or oil-containing materials. Where known, test results set forth below include the weight percent of grease, fat or oil in the subject materials. However, since some tested product were proprietary formulations, the amount of grease, fat or oil within the product was unknown. In such cases, grease, fat or oils that may be present in the tested product are described.

10

à.

-	Pigment	68.8%		Protein %	later %	•		Total % comb. Binder.	Parslatex	Parts protein Marian
	· pigments	47.6%	52.4%	3.8%	27.3%	0.09%	,	* all w	966	2,0
	dry lbs	10.2	11.25	1.2	%	0.029	0	31.18	25%	,
	wet lbs	. 15	15	ø	17	0.038	\$	60.04	calc. Solids	•
	% solids	0.68	0.75	0.15	. 50	0.76	•	•		
	Product name	KaoPrint	RR-BC slurry	Pro-Cote 427	Res 3083.	Nalco 8669	•			٠.
ethod	Supplier	Theile Kaolin Company	Trioxide Americas, Inc.	Protein Technologies	Rohm & Haas	Nalco Chemical Company				
Air Coating Method	Material	Kaoline clay	TiO2	Protein	Latex	Defoamer	Water			

	Γ				•	1				
	its Pigment	68.9%					0.05%			% Binder
•	dry pigmer	45.8%	45.8%	7.8%	99.0	31.0%	0.05%	0.00%		31.0%
٠	dry lbs.	10.2	10.2		0.13	•				32.30
, .	wet Ibs	15	15	2.3	0.16	8	0.02	0.078	8 0	57.6
	spilos %	89.0	0.68	0.75	8.0	0.5	0.76	0.354	0	•
· · ·	· Product name	Kaobrite	KaoPrint	RR-BC slurry	FDA listed pigment	Res 3083	Nalco 8669	Alcogum 149		-
thod	Supplier	Theile Kaolin Company	Theile Kaolin Company	Trioxide Americas, Inc.	Various	Rohm & Haas	Nalco Chemical Company	Alco Chemical		•
TABLE 2 Rod Coating Me	Material	Kaoline clay #1	e clay #2	-	Black	Latex	Defoamer	Thickener	Water	

TABLE 3: COATING FORMULATIONS TESTED

[·		Coating	Cooting	Cooting	G-4	C=-43
}	Coating	Formula	Coating Formula	Coating Formula	Coating	Coating
	Formula #1	#1A	#1C	#1D	Formula #2A	Formula #2 B
First Down	Politica #1	WIR	#10	#110	#ZA	#2.15
(White/light)						
Top Coating(s)						
Pigments						
Kaolin Clay 1	28.7%	35.2%	35.2%	35.2%	35.2%	35.2%
Kaolin Clay 2	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
TiO2	71.3%	29.1%	29.1%	29.1%	29.1%	29.1%
Total Pigment %	63.0%	64.3%	64.3%	64.3%	64.3%	64.3%
Binders		0	01.570	0-1.570	04.570	04.576
Soy Protein	2.5%	0.0%	0.0%	0.0%	0.0%	0.0%
Poly vinyl acetate		0.070	0.070	0.070	0.078	0.076
latex	34.1%	35.6%	35.6%	35.6%	35.6%	35. 6%
Total % comb.			55.676	33.070	33.070	33.076
Binder	36.6%	35.6%	35.6%	35.6%	35.6%	35.6%
Additives					33.070	33.070
Thickener	0.07%	0.0%	0.0%	0.0%	0.0%	0.0%
Alcosperse	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%
Defoamer	0.25%	0.0%	0.0%	0.0%	0.0%	0.0%
First down						3,3,0
(dark) coating			,			
Starch Cationic	5%	0	0	0	0	0
Black Pigment	0.6%	0.1%	0.2%	0.2%	0.51%	0.51%
Water	94.40%	0.0	0	0	0	0
Pigments						
Kaolin Clay 1	0%	0.0%	0.0%	0.0%	0.0%	0.0%
Kaolin Clay 2	0%	64.6%	64.6%	57.0%	60.3%	60.3%
TiO ₂	0%	0.0%	0.0%	11.1%	6.4%	6.4%
Total Pigment %	0%	64.6%	64.6%	68.1%	66.6%	66.6%
Binders						
Soy Protein	0	0.0	0.0	0.0	0.0	0.0
Poly vinyl acetate						
Latex	0.0	35.3%	35.2%	31.7%	32.8%	32.8%
Total % comb.						
Binder	0%	35.3%	35.2%	31.7%	32.8%	32.8%
Additives	0	0	. 0	0	0	0
Thickener		0	0	0	0	0
Dispersant	0	0	0	0	0	0
Defoamer	0	0	0	0	0	0

andre Sylvisia

127 - 18

and the second s

Table 3 CONT.

Table 3 CONT	•		•			
	Coating Formula #2C	Coating Formula #5	Coating Formula #6	Coating Formula #7	Coating Formula #7-4B	Coating Formula
First Down				- "'-	#/-4.D	#8
(White/light)]		
Top						
Coating(s)						l
Pigments						
Kaolin Clay 1	35.2%	35.2%	17.6%	44.90%	44.9%	44.9%
Kaolin Clay 2	0.0%	0.0%	0.0%	7 112 370	17.276	44.9%
TiO2	29.1%	29.1%	46.6%	18.1%	18.1%	19 10/
Total Pigment				101270	10.178	18.1%
%	64.3%	64.3%	64.2%	63.0%	63.0%	63.0%
Binders					03.076	03.0%
Soy Protein	2.0%	2.9%	0.0%	2.5%	2.5%	2.5%
Poly vinyl					2.576	2.3%
acetate latex	33.0%	31.0%	35.6%	34.1%	34.1%	3/110/
Total %	-			33270	34.170	34.1%
comb. binder	35.0%	33.9%	35.6%	36.6%	36.6%	36.6%
Additives			·		20.076	30.076
Thickener	0.0%	0.31%	0.065%	0.07%	0.07%	0.07%
Dispersant	0.0%	0.16%	0.12%	0.10%	0.10%	0.10%
Defoamer	0.0%	0.04%	0.007%	0.25%	0.25%	0.25%
First down			·		0.2370	0.23%
(dark) coating						
Starch Cationic	0	0	0	0	5%	5%
Black Pigment	0.51%	0.15%	0.15%	0.2%	0.6%	
Water	0	0.0	0.0	0.0	94.41)%	0.6%
Pigments					24.4976	94.40%
Kaolin Clay 1	0.0%	31.0%	29.9%	30.2%	0%	0%
Kaolin Clay 2	60.3%	31.0%	29.9%	30.2%	0%	0%
TiO ₂	6.4%	5.0%	5.1%	5.1%	0%	. 070
Total Pigment					073	0%
%	66.6%	67.0%	64.9%	65.5%	0%	007
Binders					070	0%
Soy Protein	0.0	0.0-	0.0		0	
Poly vinyl						0
acetate Latex	32.8%	32%	35%	34%	0.0	0.0
Total %					- 0.0	0.0
comb. Binder	32.8%	32.0%	35.2%	34.0%	0%	0%
Additives	0				0/6	
Thickener	0	0.31%	0.15%	0.21%	0	0
Dispersant	0	0.16%	0.10%	0.00%	0	0

	Coating Formula #2C	Coating Formula #5	Coating Formula #6	Coating Formula #7	Coating Formula #7-4B	Coating Formula #8
Defoamer	0	0.04%	0.15%	0.04%	0	0

TABLE 4: Masking of Packaging Material Contacted with Votive Candles or Oil

Impregnated Dusting Gloves

Substrate	Votive Candles*	Oil impregnated Dusting Glove (~5% mineral oil)
Coating Formula 1 Stack test Stored at 120 deg F Evaluated at 31 days	Good – No outside staining and very little inside staining	
Coating Formula 1 Carton test Stored at 120 deg F Evaluated at 117 days		Good - No outside staining; very little to no inside staining
Coating Formula 1 Carton test Stored at TAPPI conditions (73 deg. F, 50% humidity) Evaluated at 117 days		Good - No outside staining; very little to no inside staining

^{*} Composition of votive candles unknown. Such candles are known to include petroleum (oily) waxes and fragrance oils.

TABLE 5: Masking of Packaging Materials Contacted with Various Cat Food Formulations

Substrate	Cat Food Formula I (≥10% Fat Content)	Cat Food Formula II (≥14% Fat Content)
Coating Formula 1 Hand filled Carton test Stored at 120 deg F Evaluated at 61 days Coating Formula #7-4B Pile test Stored at 120 deg F Evaluated at 117 days	Good — No ourtside staining; Moderate inside staining; no staining to corrugated under carton	Good – No outside staining; Moderate inside staining; no staining to corrugated under carton Good – No outside staining; Moderate inside staining
CCNB (comparative) Pile test Stored at 120 deg F Evaluated at 21 days	Poor staining	Poor staining

Substrate	Tour	
Substrate	Cat Food Formula I	Cat Food Formula II
Low do not Division	(≥10% Fat Content)	(≥14% Fat Content)
Low density Polyethylene Extruded CCNB	Poor - Inside edge wicking	Poor - Inside edge wicking
		3
Paperboard Clear Inside		
Poly (½ mil inside)		
(comparative)	· ·	
Stored at 120 deg F		
Evaluated at 21 days	·	
White Outside low density	Poor - Outside staining	Poor - Outside staining
Polyethylene extrusion	visible	visible
coated CCNB -	! ·	
(comparative)	1	
Stored at 120 deg F	1.	
Evaluated at 21 days		
White 2-sided low density	Poor - Inside edge wicking	Poor - Inside edge wicking
Polyethylene extrusion		more odge wicking
coated CCNB		
(comparative)		
Stored at 120 deg F	·	
Evaluated at 21 days		
Metalized Polyester Film	Good - Inside staining, no	Good - Inside staining, no
laminated to CCNB	outside staining	outside staining
(comparative)		J. J
Stored at 120 deg F		
Evaluated at 21 days		
Coating Formula #1A, 1C,	Good - Slight inside	
1D Stored at 120 deg F	staining, no outside staining	Good - Slight inside stain;
Evaluated at 21 days	ommig, no outside staining	shiny area on outside where
		product was piled (not a
PM	Good – Inside edge	stain appearance)
Stored at 120 deg F	Wicking no outside at the	Good - Inside edge
Evaluated at 21 days	wicking, no outside staining	wicking, no outside staining
		`

TABLE 6: Masking of Packaging Materials Contacted with Various Dog Snack

Formulations					
Substrate	Dog Snacks Formula 1 (≥4% Fat content)	Dog Snacks Formula II (≥3% Fat content)	Dog Snacks Formula III (≥6% Fat content)	Dog Snacks Formula IV (≥6% Fat content)	Dog Snacks Formula V (≥14% Fat content)
Coating Formula 1 Machine filled Carton test Stored at 120 deg F Evaluated at 61 days			:		Good – No outside stains; moderate inside staining
RF2 (comparative) Machine filled Carton Test Stored at 120 deg F Evaluated at 61 days					Poor – Moderate staining seen on printed side; moderate inside staining
Coating Formula 1 Hand filled carton test Stored at 120 deg F Evaluated at 72 days				Good – No outside staining; no staining on corrugated under carton	Good – No outside staining; moderate inside staining; no staining to corrugated under carton

Substrate	Dog Snacks	Dog Snacks	Dog	Dog	150
	Formula 1	Formula II	Snacks	Snacks	Dog
: ,	(≥4% Fat	(≥3% Fat	Formula		Snacks
i ₄ :	content)	content)	III	Formula	Formula V
.:	- Contoney	content	1	IV	(≥14% Fat
			(≥6% Fat	(≥6% Fat	content)
RF2	<u> </u>	 	content)	content)	<u> </u>
(comparative)				Poor –	Poor -
Test				Several	Many oil
Stored at 120				stains on	droplet
deg F		~		printed	stains on
Evaluated at 72				side; no	printed
days				staining to	side;
		1		corrugated	moderate
- **		, ·		under	inside .
				carton	staining, no
					staining to
	,			ļ.	corrugated
•		```	1	ļ	under
Coating					carton
Formula #7-4B				ŀ	Good - no
Pile test				1	outside
Stored at 120					staining
deg F		÷		İ	moderate
Evaluated at		-			inside
117 days					staining
CCNB	Good - No	Good - No	Marginal –	D- 1/22	
(comparative)	inside or	inside or	No major	Poor - 1/4"	Poor –
Hand-filled	outside	outside	staining,	stains in	Staining all
cartons Stored	staining	staining	several	several	over the
at 120 deg F		Juning	small spots	areas of the	outside of
Evaluated at 21			of staining	carton	the carton
days		a.e	or starring		·
Low density	Good - No	Good - No	Good - No	Good - No	7
Polyethylene	edge	edge	edge		Poor –
Extruded (1/2	wicking or	wicking or	wicking or	edge wicking or	Edge
mil inside)	staining	staining	staining		staining
CCNB		8	- commig	staining	<u> </u>
Paperboard			•		
(comparative)		İ			
Pile Test					٠
Stored at 120		Ì		1	
deg F		ļ			
Evaluated at 21					
days					

Substrate	Dog Snacks Formula 1 (≥4% Fat content)	Dog Snacks Formula II (≥3% Fat content)	Dog Snacks Formula III (≥6% Fat content)	Dog Snacks Formula IV (≥6% Fat content)	Dog Snacks Formula V (≥14% Fat content)
Coating Formula #1D Pile test Stored at 120 deg F Evaluated at 21 days	Good – No	Good – No	Good – No	Good – No	Good – No
	outside	outside	outside	outside	outside
	staining	staining	staining	staining	staining
PM Pile Test Stored at 120 deg F Evaluated at 21 days	Good – No	Good – No	Good – No	Good – No	Good – No
	outside	outside	outside	outside	outside
	staining	staining	staining	staining	staiming

TABLE 7: Masking of Packaging Materials Contacted with Hand Lotion*

Substrate	Lotion Drop Test (7 hours)	Lotion Stack Test (3 weeks)	Lotion Product Storage Test (3 weeks)
Coating Formula #8 Hand filled Carton Stored at 120 deg F	Good – No outside staining	Good – No outside staining	Good – No outside staining
Coating Formula #7- 4B Stored at 120 deg F	Good – No outside staining	Good – No outside staining	·
Coating Formula #6 Stored at 120 deg F	Good – No outside staining	Good – No outside staining	
Coating Formula #5 Stored at 120 deg F	Good – No outside staining	Good – No outside staining	
Coating Formula #2A, 2B, 2C Stored at 120 deg F	Good – No outside staining	Good – No outside staining	
Coating Formula #1- 1A, 1B, 1C Stored at 120 deg F	Good – No outside staining	Good – No outside staining	·

^{*} Lotion formulation unknown, but hand lotions known to contain moderate amounts of oils, including mineral oil.

TABLE 8: Masking of Packaging Materials Contacted with Biscuit Mix Substrate Biscuit Mix (>140/ Find G)	
	Biscuit Mix (≥14% Fat Content)
Coating Formula 1	Good - No outside staining; Light inside staining; no
Hand filled carton test	staining to corrugated under carton
Stored at 120 deg F	·
Evaluated at 72 days	
RF1 (comparative)	Good - No outside staining; no staining to corrugated
Machine filled Carton test	under carton
Stored at 120 deg F	
Evaluated at 72 days	<u></u>
Coating Formula #7-4B	Good - No outside staining, Light inside staining
Pile Test	ByBit more during
Stored at 120 deg F	· ·
Evaluated at 117 days	
CCNB (comparative)	Poor staining
Pile test Stored at 120 F	
Evaluated at 26 days	
Low density Polyethylene	Good - No staining or edge wicking
Extruded CCNB Paperboard	or order whoming
(1/2 mil inside) (comparative)	
Pile Test	
Stored at 120 deg F	
Evaluated at 26 days	
GM (comparative)	Poor - Light staining through the board
Pile test	S Summing untough the boatd
Stored at 120 deg F	
Evaluated at 26 days	
2 sided White Low density	Good - No staining or edge wicking
Poly CCNB (comparative)	
Pile Test	
Stored at 120 deg F	·
Evaluated at 26 days	
White outside Poly	Poor - Significant staining
(comparative)	
Pile Test	
Stored at 120 deg F	·
Evaluated at 26 days	

TABLE 9: Masking of Packaging Materials Contacted with Lotion Impregnated Tissues*

Substrate	Lotion-containing Tissues
Coating Formula 1	Good - No outside
Hand filled carton Test Stored at 120 F	staining
Evaluated at 72 days	
Coating Formula 1	Good - No outside
Hand filled carton Test	staining
Stored at TAPPI conditions (73 deg. F, 50% humidity)	
Evaluated at 72 days	

^{*} Amount and formulation of lotion in tissues unknown, but lotion compositions known to contain moderate amounts of oils, including mineral oils.

TABLE 10: Masking of Packaging Materials Contacted with Various Cat Food Formulations

Formulations		
Substrate	Cat Formula III	Cat Food Formula IV
	(≥14% Fat content)	(≥12% Fat content)
Coating Formula 1	Good - No outside staining;	
Carton test Stored at 120 F	moderate inside staining;	,
Evaluated at 72 days	moderate staining at one	
	corner of carton to	
	corrugated under carton	
Coating Formula #7-4B		Good - No outside staining;
Piled test Stored at 120 F		moderate inside staining
Evaluated at 117 days		
CCNB (comparative)	Poor – Inside and outside	Poor - Inside and outside
Piled Test Stored at 120 F	staining	staining
Evaluated at 183 days		
Coating Formula #2C	Good - No outside staining	Good - No outside staining
Piled test Stored at 120 F		_
Evaluated at 183 days		

TABLE 11: Masking of Packaging Materials Contacted with Various Cat Food Formulations

Substrate	Cat Food Formula V (≥8% Fat Content)
Coating Formula 1 Carton test Stored at 120 F Evaluated at 72 days	Good – No outside staining; Heavy staining on inside of carton; Heavy staining on corrugated under the carton
RF2 (comparative) Pile test Stored at 120 F Evaluated at 117 days	Marginal — No inside staining; slight staining on printed side of sample

Coating Formula #7-4-B Piled test Stored at 120 F Evaluated at 117 days	Good – No outside staining; Heavy staining on inside of paperboard
Low density Polyethylene Extruded CCNB Paperboard (½ Mil inside) (comparative) Hand-filled carton test Stored at 120 F Evaluated at 21 days	Poor – Pin-holing staining on carton; heavy edge wicking staining
Coating Formula #2A, 2B, 2C Filled Carton test Stored at 120 F Evaluated at 36 days	Good – No outside staining; Heavy staining on fiber side of paperboard; Staining on paperboard under the sample
Coating Formula #2A, 2B, 2C Piled test Stored at 140 F Evaluated at 14 days	Good – No outside staining; Heavy staining on fiber side of paperboard

TABLE 13: Masking of Packaging Materials Contacted with Gravy Mix, Pancake Mix and Biscuit Mix

Mix and Biscuit Mix			
Substrate	Gravy Mix (~10% Fat Content)	Pancake Mix (~3% Fat Content)	Biscuit Mix II (≥3% Fat Content)
Coating Formula #7-4B Pile Test Stored at 120 F Evaluated at 117 days Low density Polyethylene Extruded CCNB Paperboard (1/2 mil inside) (comparative) Filled Carton Test Stored at 120 F Evaluated at 154 days	Good - No outside staining, Light inside staining Good - No staining or edge wicking; Very slight staining seen after 4 months, however, print graphics would likely cover the stain; Staining at die cut edges and along bottom fold is		
CCNB (comparative) Filled Carton Test Stored at 120 F Evaluated at 154 days	worsening in the 5 th month of storage	Good – No staining or edge wicking	
CCNB (comparative) Pile Test Stored At 120 Deg F Evaluated at 24 days	Poor- Major staining	Good - No staining or edge wicking	Good - No staining or edge wicking
Low density Polyethylene Extruded CCNB Paperboard (1/2 mil inside) (comparative) Pile Test Stored at 120 F Evaluated at 28 days	Good – No staining	Good – No staining	Good – No staining
PM (comparative) Pile Test Stored at 120 F Evaluated at 28 days	Good - No staining to the print side	Good - No staining	Good – No staining

Table 14: Masking of Packaging Materials Contacted with Snack Crackers and Dog Riscuits

Substrate	Snack Crackers (~16% Fat content)	Dog Biscuits (~6% fat Content)
Coating Formula 1 Hand filled carton Test without inner liner Stored at 120 deg F Evaluated at 22 days		Good – No outside staining, no inside staining
Coating Formula 1 Hand filled carton Test without inner liner Stored at 120 deg F Evaluated at 72 days	Good – No outside staining, very slight staining to corrugated at	: :
Coating Formula 1 Hand filled carton Test without inner liner Stored at 140 deg F Evaluated at 72 days	Good – No outside staining, very slight staining to corrugated at	
Coating Formula 1 Hand filled carton Test without inner liner Stored at TAPPI conditions (73 deg. F, 50% humidity) Evaluated at 72 days	Good – No outside staining, no staining to corrugated under carton	10 mm 10 mm
RF2 without inner liner (comparative) Stored at 120 F Evaluated at 72 days	Good – No outside staining, medium staining to corrugated at	
RF2 (comparative) Stored at 140 F Evaluated at 72 days	Good – No outside staining, medium staining to corrugated at	:
RF2 (comparative) TAPPI conditions (73 d eg. F, 50% humidity) Evaluated at 72 days	Good – No outside staining, no staining to corrugated under carton	
Coating Formula #2A, 2B, 2C Pile Test Stored at 140 deg. F at 14 days	Good – No Staining	

TABLE 15: Masking of Packaging Materials Contacted with Various Dryer Sheets*

Substrate	Dryer	Dryer Sheet	Dryer Sheet III	Dryer Sheet
	Sheet I	П		IV
Coating Formula 1	Good -	Good – No	Good - No	Good - No
Hand-filled Carton test	No	outside	outside staining	outside
Stored at 120 F	outside	staining		staining
Evaluated at 4 days	staining	٠		
Coating Formula 1	Good -	Good – No	Good – No	Good - No
Hand-filled Carton test	No	outside	outside staining	outside
Stored at 100 F / 70%	outside	staining		staining
RH	staining			, -
Evaluated at 4 days				
Coating Formula 1	Good -	Good - No	Good - No	Good - No
Hand-filled Carton test	No	outside	outside staining	outside
80 deg F / 80% RH	outside	staining		staining
Evaluated at 4 days	staining			
Coating Formula 1	Good –	Good - No	Good - No	Good - No
Hand-filled Carton test	No	outside	outside staining	outside
Stored at TAPPI	outside	staining		staining
conditions (73 deg. F,	staining			
50% humidity)				
Evaluated at 4 days		<u>:</u>		
Low density	Good -	Poor – Major	Marginal -	Good - No
Polyethylene Extruded	No	outside	Slight outside	outside
(1/2 mil inside) CCNB	outside	staining	staining around	staining
Paperboard	staining	around die cut	perforations	· ·
(comparative)	1	perforations		1 ·
Hand-filled carton test		}		
Stored at 120 F		·	•	
Evaluated at 4 days				
Low density	Good -	Good – No	Good - No	Good - No
Polyethylene Extruded	No	outside	outside staining	outside
(1/2 mil inside) CCNB	outside	staining		staining
Paperboard	staining			
(comparative)	ļ			
Hand-filled carton test	1			
Stored at 100 F / 70%				
RH	1			
Evaluated at 4 days	<u> </u>			<u> </u>

Substrate	Dryer Sheet I	Dryer Sheet	Dryer Sheet III	Dryer Sheet
Low density Polyethylene Extruded (1/2 mil inside) CCNB Paperboard (comparative) Hand-filled carton test Stored at 80 deg F / 80% RH Evaluated at 4 days	Good – No outside staining	Good – No outside staining	Good – No outside staining	Good — No outside staining
Low density Polyethylene Extruded (1/2 mil inside) CCNB Paperboard (comparative) Hand-filled carton test Stored at TAPPI conditions (73 deg. F, 50% humidity) Evaluated at 4 days	Good – No outside staining	Good – No outside staining	Good – No outside staining	Good — No outside staining
Coating Formula 1 Stack test – Stored at 120 F Evaluated at 7 days	Good – No staining to print side; slight tack on print to print stack test	Poor — Heavy tack on print to print stack test*	Good – No staining to print side; slight tack on print to print stack test	Good — No staining to print side; slight tack on print to print stack test

^{*} Composition of dryer sheets unknown. However, commercial dryer sheets are known to be impregnated with fabric softener compositions. Such compositions are known to include one or more of: fatty alcohols, mineral oils, or organosilicone materials.

As set forth in the various Tables above, the substrates treated according to the methods and compositions and methods of the present invention effectively mask staining from grease, fat or oil permeation through a packaging material. Further, the appearance of the packaging material is equal to or better than packaging materials treated according to prior art methods and compositions including the now unavailable flurochemical barrier treatments. Accordingly, these results demonstrate that the

methods and compositions of the present invention provide a useful and waluable improvement to the field of packaging materials.

Throughout this application, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this invention pertains.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

12.0

What is claimed is:

- 1. A material for packaging grease, fat or oil-containing substances, wherein the material comprises:
 - a. a grease, fat or oil permeable substrate suitable for use as a packaging material, wherein the substrate has an inner and an outer surface;
 - b. a dark colored layer comprising a dark colorant and having an inner and an outer surface, wherein the dark colored layer is optionally applied from a solution comprising a dark colorant, and wherein the inner surface of the dark colored layer is disposed proximal to the outer surface of the substrate; and
 - c. a light colored layer having an inner and an outer surface, wherein the light colored layer is applied from a solution comprising a light colorant, and wherein the inner surface of the light colored layer is disposed proximal to the outer surface of the dark colored layer;

wherein one or more of the light colored or dark colorant-containing solutions each, independently, comprises a binder material at from about 17 % to about 60 % by weight of the respective colorant-containing solution, wherein the dark and light colored layers are selected to mask an appearance of grease, fat or oil staining on the packaging material, and wherein neither the dark colored layer nor the light colored layer comprises a non-leafing metallic ink.

- 2. The packaging material of claim 1, wherein the inner surface of the light colored layer is adjacent to the outer surface of the dark colored layer.
- 3. The packaging material of claim 1, wherein the inner surface of the dark colored layer is adjacent to the outer surface of the substrate.
- 4. The packaging material of claim 1, wherein the dark colorant comprises one or

more of: carbon black, raw sienna, burnt sienna, burnt umber, chrome black, high purity furnace black, black azo dyes or brown azo dyes.

- 5. The packaging material of claim 1, wherein the dark colorant comprises carbon black.
- 6. The packaging material of claim 1, wherein the light colorant comprises one or more of: titanium dioxide, calcium carbonate, calcium silicate, calcium sulfate, barium sulfate, natural clay, synthetic clay, magnesium oxide, magnesium silicate, zinc carbonate, zinc oxide or plastic pigment.
- 7. The packaging material of claim 1, wherein the light colorant comprises titanium dioxide.
- 8. The packaging material of claim 1, wherein the dark colored layer is applied from the dark colorant-containing solution and the solution comprises from about 0.01 to about 20.0 % by weight of the dark colorant as measured by total weight of the solution.
- 9. The packaging material of claim 1, wherein the dark colored layer is applied from the dark colorant-containing solution and the solution comprises from about 0.25 to about 4.0 % by weight of the dark colorant as measured by total weight of the solution.
- 10. The packaging material of claim 1, wherein the light colorant-containing solution comprises from about 30 to about 90 % by weight of the light colorant as measured by total weight of the solution.
- 11. The packaging material of claim 1, wherein the light colorant-containing solution comprises from about 40 to about 80 % by weight of the light colorant as measured by total weight of the solution.
- 12. The packaging material of claim 1, wherein the substrate comprises one or more dark colored outer plys, thereby providing the dark colored layer on the outer

- surface of the substrate.
- 13. The packaging material of claim 1 having a TAPPI brightness number of from about 60 to about 90.
- 14. The packaging material of claim 1, wherein the dark colored layer is applied from the dark colorant-containing solution and the solution further comprises a sizing agent, dark colored pigment and water.
- 15. The packaging material of claim 14, wherein the sizing agent comprises starch.
- 16. The packaging material of claim 1, wherein the grease, fat or oil permeable substrate comprises paperboard, paper or fabric.
- 17. The packaging material of claim 1, wherein the grease, fat or oil permeable substrate comprises paperboard.
- 18. The packaging material of claim 17, wherein the paperboard comprises one or more of: SBS, SUS or recycled paperboard.
- 19. The packaging material of claim 1, wherein the packaging material is suitable for use in packaging of human food, animal food, drugs or cosmetics.
- 20. The packaging material of claim 1, wherein one or more of the dark or the light colorant-containing solutions each, independently, further comprise one or more of: water, dispersant, resin, surfactant, wetting agent, defoamer, thickener, starch, preservative or antioxidant.
- 21. The packaging material of claim 1, wherein the binder is present at from about 20 to about 50 % by weight of the light or dark colorant-containing solutions.
- 22. The packaging material of claim 1, wherein the binder comprises one or more of a naturally or synthetically derived binder.
- 23. The packaging material of claim 1, wherein the binder comprises a latex

- polymer and a protein.
- 24. The packaging material of claim 23, wherein the ratio of latex polymer to protein is from about 2:1 to about 10:1.
- 25. The packaging material of claim 1, further comprising a printed layer adjacent to the outer surface of the light colored layer.
- 26. An article prepared from the packaging material of claim 1.
- 27. The article of claim 26, wherein the article further comprises a consumer good.
- 28. The article of claim 26 in the form of a wrap, pouch, bag, box, cup, tray, plate, can, tube or bottle.
- 29. The article of claim 26, further comprising a food material comprising one or more of: sweets, chocolate, confectionery, pastries, biscuits, dairy products, powdery foodstuffs, frozen food, fresh and semipreserved foods, pet food, or carryout foods.
- 30. The article of claim 26, further comprising a non-food material comprising one or more of: cosmetics, toiletries, pharmaceuticals, cigarettes, detergents, textiles, toys, games, tools, household appliances, pesticides, fertilizers, hobby items, paper products, cassettes, record sleeves, or auto parts.
- 31. A material for packaging grease, fat or oil-containing substances, wherein the material comprises:
 - a. a grease, fat or oil **pe**rmeable substrate suitable for use as a packaging material, wherein the substrate has an inner and an outer surface;
 - b. a dark colored layer comprising a dark colorant and having an inner and an outer surface, wherein the dark colored layer is optionally applied from a composition comprising a dark colorant, and wherein the inner surface of the dark colored layer is disposed proximal to the outer surface of the

substrate; and

c. a light colored layer having an inner and an outer surface, wherein the light colored layer is applied from a composition comprising a light colorant and one or more of: polyethylene, polypropylene, polyester, polystyrene, or halogenated or non-halogenated vinyl polymer, and wherein the inner surface of the light colored layer is disposed proximal to the outer surface of the dark colored layer;

wherein the dark and light colored layers are selected to mask an appearance of grease, fat or oil staining on the packaging material, and wherein neither the dark colored layer nor the light colored layer comprises a non-leafing metallic ink.

- 32. The packaging material of claim 31, wherein the dark colored layer is applied from the dark colorant-containing composition and the dark and light colored compositions each, independently, comprise from about 5 to about 40 % colorant as measured by the total weight of each colored composition.
- 33. The packaging material of claim 31, wherein the dark colored layer is applied from the dark colorant-containing composition and the composition comprises one or more of: polyethylene, polypropylene, polyester, polystyrene, or halogenated or non-halogenated vinyl polymer.
- 34. An article prepared from the packaging material of claim 31.
- 35. The article of claim 34 in the form of a wrap, pouch, bag, box, cup, tray, plate, can, tube or bottle.
- 36. The article of claim 34 further comprising a consumer good.
- 37. The article of claim 34 further comprising a food material comprising one or more of: sweets, chocolate, confectionery, pastries, biscuits, dairy products,

٠. .

powdery foodstuffs, frozen food, fresh and semipreserved foods, pet food, or carryout foods.

- 38. The article of claim 34 further comprising a non-food material comprising one or more of: cosmetics, toiletries, pharmaceuticals, cigarettes, detergents, textiles, toys, games, tools, household appliances, pesticides, fertilizers, hobby items, paper products, cassettes, record sleeves, or auto parts.
- 39. A material for packaging grease, fat or oil-containing substances, wherein the material comprises:
 - a. a grease, fat or oil permeable substrate suitable for use as a packaging material, wherein the substrate has an inner and an outer surface;
 - b. a dark colored layer comprising a dark colorant and having an inner and an outer surface, wherein the dark colored layer is optionally applied from a solution comprising a dark colorant, and wherein the inner surface of the dark colored layer is disposed proximal to the outer surface of the substrate; and
 - c. a light colored layer having an inner and an outer surface, wherein the light colored layer is applied from a solution comprising a light colorant, and wherein the inner surface of the light colored layer is disposed proximal to the outer surface of the dark colored layer;

wherein one or more of the light colored or dark colorant-containing solutions each, independently, comprises a binder material at from about 17 % to about 60 % by weight of the respective colorant containing solution, wherein the dark and light colored layers are selected to mask an appearance of grease, fat or oil staining on the packaging material, and wherein both the dark colorant and light colorant containing solutions are aqueous.

40. The packaging material of claim 39, wherein neither the dark colored layer nor

the light colored layer comprises a non-leafing metallic ink.

41. The packaging material of claim 39, wherein the dark colored layer is applied from the dark colorant-containing solution and the solution comprises a sizing agent, dark colored pigment and water.

- 42. The packaging material of claim 39, wherein the sizing agent comprises starch.
- The packaging material of claim 39, wherein the grease, fat or only permeable substrate comprises paperboard, paper or fabric.
- The packaging material of claim 43, wherein the substrate comparises paperboard comprising one or more of: SBS, SUS or recycled paperboard.
 - The packaging material of claim 39, wherein the packaging material is suitable for use in packaging human food, animal food, drugs or cosmetics.
 - 46. The packaging material of claim 39, wherein the binder comprises one or more of: a naturally or a synthetically derived binder.
- 47. The packaging material of claim 39, wherein the binder comprises a latex polymer and a protein.
 - 48. The packaging material of claim 47, wherein the ratio of latex polymer to protein is from about 2:1 to about 10:1.
 - 49. An article prepared from the packaging material of claim 39.
 - The article of claim 49, in the form of a wrap, pouch, bag, box, cup, tray, plate, can, tube or bottle.
 - 51. The article of claim 49 further comprising a consumer good.
 - 52. The article of claim 49 further comprising a food material comprising one or more of: sweets, chocolate, confectionery, pastries, biscuits, dairy products,

powdery foodstuffs, frozen food, fresh and semipreserved foods, pet food, or carryout foods.

- The article of claim 49 further comprising a non-food material comprising one or more of: cosmetics, toiletries, pharmaceuticals, cigarettes, detergents, textiles, toys, games, tools, household appliances, pesticides, fertilizers, hobby items, paper products, cassettes, record sleeves, or auto parts.
- 54. A method of making a packaging material that masks grease, fat or oil permeation in a grease, fat or oil permeable packaging material comprising the steps of:
 - a. providing a grease, fat or oil permeable substrate suitable for use as a packaging material, wherein the substrate has an inner and an outer surface;
 - b. selecting a dark colored layer having an inner and an outer surface and a light colored layer having an inner and an outer surface, wherein the layers are together suitable for masking an appearance of a grease, fat or oil permeation on the packaging material;
 - applying the dark colored layer proximal to the outer surface of the substrate, wherein the dark colored layer is optionally applied from a solution comprising a dark colorant; and
 - d. applying the light colored layer proximal to the outer surface of the dark colored layer, wherein the light colored layer is applied from a solution comprising a light colorant;

wherein one or more of the dark or light colorant-containing solutions each, independently, comprises a binder material at from about 17% to about 60% by weight as measured by weight of the respective solution, and wherein neither the dark colored layer nor the light colored layer comprises a non-leafing metallic ink.

55. The method of claim 54, wherein the inner surface of the dark colored layer is adjacent to the outer surface of the substrate.

- 56. The method of claim 54, wherein the inner surface of the light colored layer is adjacent to the outer surface of the dark colored layer.
- 57. The method of claim 54, wherein the dark colorant comprises one or more of: carbon black, raw sienna, burnt sienna, burnt umber, chrome black, high purity furnace black, black azo dyes or brown azo dyes.
- 58. The method of claim 54, wherein the dark colorant comprises carbon black.
 - 59. The method of claim 54, wherein the light colorant comprises one or more of: titanium dioxide, calcium carbonate, calcium silicate, calcium sulfate, barium sulfate, natural clay, synthetic clay, magnesium oxide, magnesium silicate, zinc carbonate, zinc oxide or plastic pigment.
 - 60. The method of claim 54, wherein the light colorant comprises titanium dioxide.
 - 61. The method of claim 54, wherein the dark colored layer is applied from the dark colorant-containing solution and the solution comprises from about 0.01 to about 20.0 % by weight of the dark colorant as measured by total weight of the solution.
 - 62. The method of claim 54, wherein the dark colored layer is applied from the dark colorant-containing solution and the solution comprises from about 0.25 to about 4.0 % by weight of the dark colorant as measured by total weight of the solution.
 - 63. The method of claim 54, wherein the light colorant-containing solution comprises from about 30 to about 90 % by weight of the light colorant as measured by total weight of the solution.

64. The method of claim 54, wherein the light colorant-containing solution comprises from about 40 to about 80 % by weight of the light colorant as measured by total weight of the solution.

- 65. The method of claim 54 having a **TAPPI** brightness number of from about 60 to about 90.
- 66. The method of claim 54, wherein the dark colored layer is applied from the dark colorant-containing solution and the solution further comprises a sizing agent, dark colored pigment and water.
- 67. The method of claim 66, wherein the sizing agent comprises starch.
- 68. The method of claim 54, wherein the grease, fat or oil permeable substrate comprises paperboard, paper or fabric.
- 69. The method of claim 54, wherein the grease, fat or oil permeable substrate comprises paperboard.
- 70. The method of claim 69, wherein the paperboard comprises one or more of: SBS, SUS or recycled paperboard.
- 71. The method of claim 54, wherein the packaging material is suitable for use in packaging human food, animal food, drugs or cosmetics.
- 72. The method of claim 54 further comparising the step of forming the packaging material into a wrap, pouch, bag, box, cup, tray, plate, can, tube or bottle, thereby forming an article.
- 73. The method of claim 72, further comprising the step of including a packaged material in the article, wherein the packaged material comprises one or more of: sweets, chocolate, confectionery, passtries, biscuits, dairy products, powdery foodstuffs, frozen food, fresh and semipreserved foods, pet food, carryout foods, cosmetics, toiletries, pharmaceuticals, cigarettes, detergents, textiles, toys,

games, tools, household appliances, pesticides, fertilizer, hobby items, paper products, cassettes, record sleeves, or auto parts.

- 74. The method of claim 54, wherein one or more of the dark colored layer and the light colored layers each, independently, comprises one or more of: water, dispersant, resin, surfactant, wetting agent, defoamer, thickener, starch, preservative or antioxidant.
- 75. The method of claim 54, wherein the binder comprises one or more of: a naturally or synthetically derived binder.
- 76. The method of claim 54, wherein the binder comprises a latex polymer and a protein.
- 77. The method of claim 76, wherein the ratio of latex polymer to protein is from about 2:1 to about 10:1.
- 78. The method of claim 54, further comprising applying a printed layer adjacent to the outer surface of the light colored layer.
- 79. A method for masking grease, fat or oil staining on a packaging material, wherein the method comprises the steps of:
 - (a) contacting the packaging material of claim 54 with a grease, fat or oil containing material.
- 80. A method of making a packaging material that masks grease and oil permeation in a grease, fat or oil packaging material, comprising the steps of:
 - a. providing a grease, fat or oil permeable substrate having an inner and an outer surface, wherein the substrate is suitable for use as a packaging material;
 - b. selecting a dark colored layer having an inner and an outer surface and a light colored layer having an inner and an outer surface, wherein the layers

- are together suitable for masking an appearance of grease, fat or oil permeation on the packaging material;
- c. extruding a composition comprising a dark colorant proximal to the outer surface of the substrate, thereby providing the dark colored layer; and
- d. extruding, either simultaneously or sequentially to step (c), a composition comprising a light colorant proximal to the outer surface of the dark colored layer, thereby providing the light colored layer.
- 81. The method of claim 80, wherein the dark colored layer and light colored layer each, independently, comprises one or more of: polyethylene, polypropylene, polyester, polystyrene or halogenated or non-halogenated vinyl polymer.
- 82. The method of claim 80, wherein the dark colored layer and the light colored layer each, independently, comprise from about 5 to about 40 % colorant as measured by total weight of each individual layer.
- 83. The method of claim 80, wherein the light colored layer comprises one or more of: titanium dioxide, calcium carbonate, calcium silicate, calcium sulfate, barium sulfate, natural clay, a synthetic clay, magnesium oxide, magnesium silicate, zinc carbonate or zinc oxide.
- 84. The method of claim 80, wherein the light colored layer comprises titanium dioxide.
- 85. The method of claim 80, wherein the substrate comprises paperboard comprising one or more of: SBS, SUS or recycled paperboard.

DNEDOCID: JAKO DODESOSOA I I

- 86. The method of claim 80, wherein the packaging material is suitable for use in packaging human food, animal food, drugs and cosmetics.
- 87. The method of claim 80 further comprising forming the packaging material into a wrap, pouch, bag, box, cup, tray, plate, can, tube or bottle, thereby forming an

article.

- 88. The method of claim 87 further comprising including a packaged material in the article comprising one or more of: sweets, chocolate, confectionery, pastries, biscuits, dairy products, powdery foodstuffs, frozen food, fresh and semipreserved foods, pet food, carryout foods, cosmetics, toiletries, pharmaceuticals, cigarettes, detergents, textiles, toys, games, tools, pesticides, fertilizers, household appliances, hobby items, paper products, cassettes, record sleeves, or auto parts.
- 89. A method for masking the appearance of grease, fat or oil staining on a packaging material, wherein the method comprises:
 - (a) contacting the packaging material of claim 80, with a grease, fat or oil containing material.
- 90. A method for making a packaging material that masks grease, fat or oil permeation in a grease, fat or oil permeable packaging material, comprising the steps of:
 - a. providing a grease, fat or oil permeable substrate having an outer surface and a dark colored outer layer having an inner and an outer surface, wherein the substrate is suitable for use as a packaging material; and
 - extruding a composition comprising a light colorant proximal to the outer surface of the dark colored outer layer, thereby providing a light colored outer layer,
 - wherein the dark colored layer and the light colored outer layer are selected so as to mask the appearance of grease, fat or oil staining on the packaging material, thereby providing a packaging material suitable for masking the appearance of grease, fat or oil on the material.
- 91. The method of claim 90, wherein the dark colored outer layer is obtained by

extruding a composition comprising a dark colorant proximal to the outer surface of the substrate prior to the extrusion step.

- 92. The method of claim 90, wherein the dark colored outer layer is obtained by applying a solution comprising a dark colorant to the outer surface of the substrate prior to the extrusion step.
- 93. The method of claim 90, wherein the dark colored outer surface is obtained by placing a dark colored paper or fabric layer on the outer surface of the substrate prior to the extrusion step.
- 94. The method of claim 90, wherein the dark colored outer surface is obtained by including one or more dark colored plys in the outer surface of the substracte prior to the extrusion step.
- 95. A method for masking grease, fat or oil staining on a packaging material method, wherein the method comprises:
 - a. contacting the packaging material of claim 90 with a grease, fat or oil containing material.
- 96. A method for making a material for masking grease and oil permeation in a grease, fat or oil permeable, substrate, comprising the steps of:
 - a. providing a grease, fat or oil permeable substrate having an inner and an outer surface, wherein the substrate is suitable for use as a packaging material;
 - b. selecting a dark colored layer and a light colored layer wherein the layers are together suitable for masking grease, fat or oil permeation in the substrate;
 - c. extruding either simultaneously or sequentially a composition comprising a dark colorant and a composition comprising a light colorant, thereby forming a laminate material having an inner and an outer surface, wherein

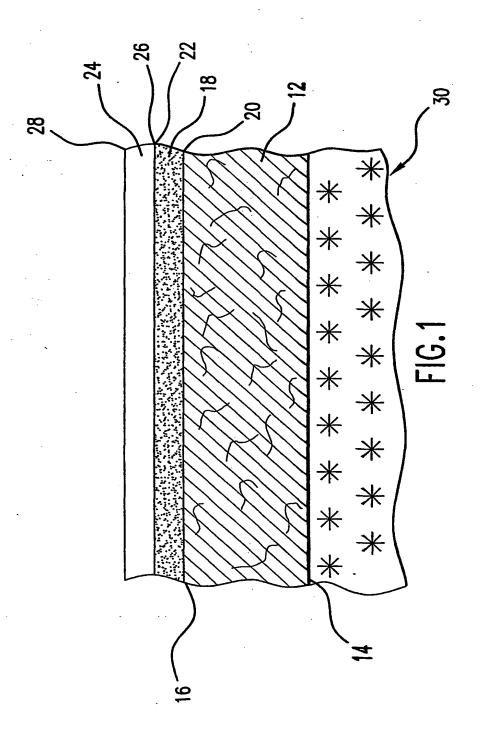
10

the light colored layer forms the outer surface of the laminate material and the dark colored layer forms the inner surface of the laminate material;

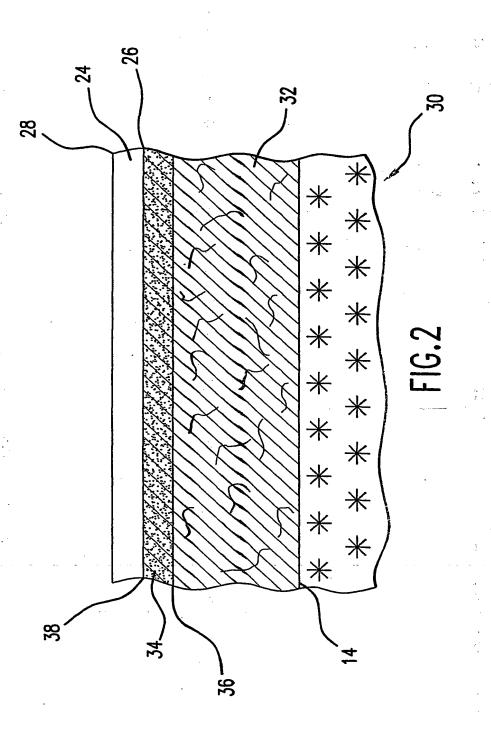
d. applying the inner surface of the laminate material to the outer surface of the substrate,

thereby providing a packaging material suitable for masking the appearance of grease, fat or oil on the material.

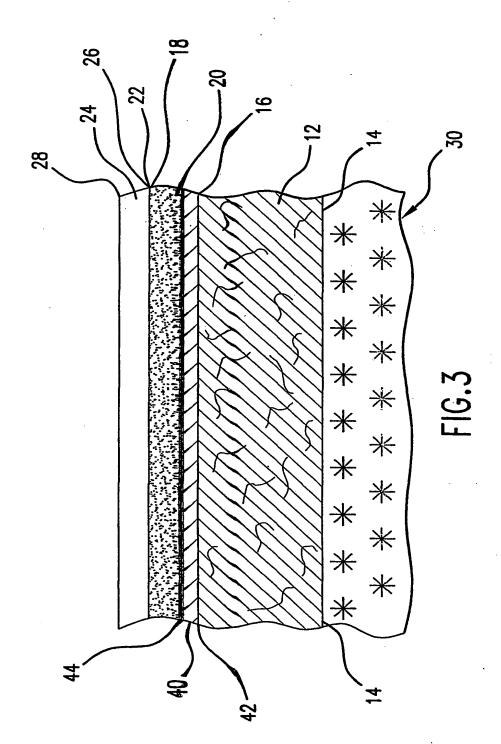
- 97. A method for masking grease, fat or oil staining on a packaging material, wherein the method comprises:
 - a. contacting the packaging material of claim 96, with a grease, fat or oil containing material.



SUBSTITUTE SHEET (RULE 26)



SUBSTITUTE SHEET (RULE 26)



SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

memational Application No PCT/US 01/50809

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 D21H27/10 D21H19/82 B32B31/30

D21H23/70

B65D65/42

B32B29/00

Relevant to claim No.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Category °

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D21H B65D B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Citation of document, with indication, where appropriate, of the relevant passages

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

- 1	1			
	Y X	US 4 521 492 A (ALLEN ROBERT L) 4 June 1985 (1985-06-04) cited in the application abstract column 3, line 47 - line 57 column 2, line 50 - line 55	 !	1,26,31, 34,54, 79,80, 89,90, 95,96 39,49
	Y	DATABASE WPI Section Ch, Week 197922 Derwent Publications Ltd., London Class A94, AN 19 79 -41571B XP002195633 & JP 54 050575 A (TAKEDA SANGYO NECTION 1979 (1979-04-20) abstract		1,26,31, 34,54, 79,80, 89,90, 95,96
ļ		her documents are listed in the continuation of box C.	Patent family members are listed	in annex.
	A docume consider the consideration that consider the consideration that consideration the consideration that consideration the consideration that consideration the consideration that consideration that consideration the consideration that	ent defining the general state of the ast which is not dered to be of particular relevance document but published on or after the international date ent which may throw doubts on priority claim(s) or is cited to establish the publication date of another or or other special reason (as specified) ent referring to an oral disclosure, use, exhibition or means ent published prior to the international tiling date but han the priority date claimed	 *T* later document published after the interpriority date and not in conflict with cited to understand the principle or the invention *X* document of particular relevance; the cannot be considered novel or cannot involve an inventive step when the document of particular relevance; the cannot be considered to involve an indocument is combined with one or ments, such combination being obvictin the art. *&* document member of the same patent 	the application but all the properties of the considered to country the considered to country the country that the country the country that the country the country that the country the country that the country
	Date of the	actual completion of the international search	Date of mailing of the international se	earch report
		10 April 2002	24/04/2002	
	Name and	mailing address of the ISA European Patent Office, P.B. 58 18 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Naeslund, P	

mternational Application No

DATABASE WPI Section Ch, Week 199218 Derwent Publications Ltd., London, Class A89, AN 1992-145229 XP002195634 & JP 04 080745 A (FUJI PHOTO FILM Class A89) 13 March 1992 (1992-03-13) abstract US 5 837 383 A (DELOZIER MORTON S 17 November 1998 (1998-11-17) cited in the application claims 1,2,6; examples 1-7	GB; O LTD),	t to claim No.
DATABASE WPI Section Ch, Week 199218 Derwent Publications Ltd., London, Class A89, AN 1992-145229 XP002195634 & JP 04 080745 A (FUJI PHOTO FILM Class March 1992 (1992-03-13) abstract US 5 837 383 A (DELOZIER MORTON S 17 November 1998 (1998-11-17) cited in the application claims 1,2,6; examples 1-7	GB; O LTD),	60,90, 9 6
Section Ch, Week 199218 Derwent Publications Ltd., London, Class A89, AN 1992-145229 XP002195634 & JP 04 080745 A (FUJI PHOTO FILM Class 13 March 1992 (1992-03-13) abstract US 5 837 383 A (DELOZIER MORTON S 17 November 1998 (1998-11-17) cited in the application claims 1,2,6; examples 1-7	GB; O LTD),	
17 November 1998 (1998-11-17) cited in the application claims 1,2,6; examples 1-7	ET AL) 1	-97
A US 4 343 858 A (THOMPSON KENNETH P) 10 August 1982 (1982-08-10) cited in the application claim 1; example 3	1	-97
DE 14 61 247 B (ASCHAFFENBURGER ZELLSTOFFWERKE AG, 8201 REDENFELDER 29 January 1970 (1970-01-29) the whole document		L -9 7
A EP 0 313 356 A (POLYCOAT AS) 26 April 1989 (1989-04-26)	:	
A US 3 463 659 A (KRASKE KARL V ET Al 26 August 1969 (1969-08-26)	.)	
AV		

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/US 01/50809

					101/03	01/50809
	atent document d in search report		Publication date		Patent family member(s)	Publication date
US 	4521492 	Α	04-06-1985	US	4568574 A	04-02-1986
JP	54050575	A 	20-04-1979	JP JP	1070070 C 56012493 B	30 -10 -198 23 -03 -198
JP	4080745	Α	13-03-1992	JP	2784840 B2	06- 08 -199
US	5837383	A	17-11-1998	US AU EP WO US US AU EP	5763100 A 3365395 A 0777575 A1 9605054 A1 5989724 A 5654039 A 6786494 A 0697961 A1 9426513 A1	09- 06 -199 07- 03 -199 11- 06 -199 22- 02 -199 23- 11 -199 05- 08 -199 12- 12 -199 28- 02 -199
US	4343858	Α	10-08-1982	NON	E , ,	
DE	1461247	В	29-01-1970	DE	1461247 B1	29 -01 -197
EP	0313356	A	26-04-1989	NO AT AU CA DE DE DE DE JP JP SU SU ZA	874385 A 91251 T 2410088 A 1331736 A1 3882197 D1 3882197 T2 583488 A ,B, 0313356 A2 2042761 T3 884841 A ,B, 1139339 A 2024482 C 7041914 B 171127 B 1836266 A3 5057359 A 8807851 A	24-04-198 15-07-199 27-04-198 30-08-199 12-08-199 03-02-199 22-04-198 26-04-198 31-05-198 26-02-199 10-05-199 23-08-199 23-08-199 26-07-198
 !!\$	3463659		26-08-1969	NON		20-07-198